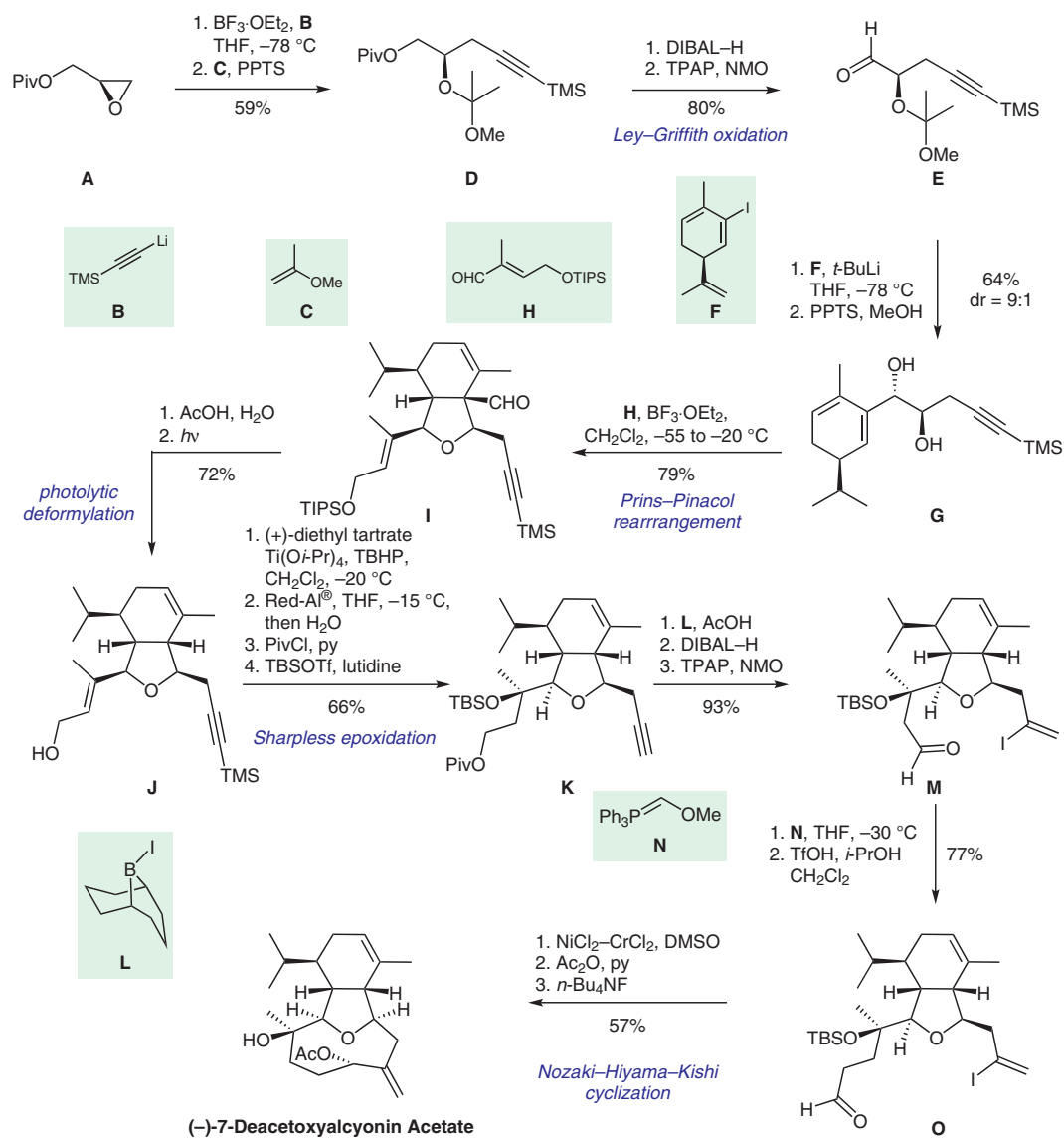


## Synthesis of (-)-7-Deacetoxyalcyonin Acetate



**Significance:** The eunicellin diterpenes feature a synthetically challenging tricyclic ring system, including a hydroisobenzofuran and oxonane subunit. MacMillan and Overman reported in 1995 the first synthesis of a member of this natural product family in asymmetric fashion, confirming the relative and absolute configuration proposed by the isolation team. Highlights of this synthesis include use of a Prins-pinacol rearrangement to access the hydroisobenzofuran core as well as a photolytic deformylation of a  $\beta,\gamma$ -desaturated aldehyde.

**Comment:** The synthesis commences with regioselective opening of **A**, which was converted into aldehyde **E** in three steps. Dienyl iodide **F** was accessed in three steps starting with (*S*)-carvone. Fusing the two fragments set the stage for Prins-pinacol rearrangement, affording **I** as a single stereoisomer. Deprotection and photolytic deformylation afforded intermediate **J**. The final oxonane ring was constructed using Nozaki-Hiyama-Kishi coupling, the natural product in two additional steps.